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Existence of a Sm-C Grain Boundary Phase at the Chiral NAC Point

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Based on a mean field analysis of the Chen-Lubensky model we extend an earlier discussion regarding the effect of chirality on the region of the phase diagram where the Cholesteric, Smectic-A, and Smectic-C* phases meet (i.e., the N* AC* point). We show that, on the Sm-C* side of the phase diagram, a second twist grain boundary (or chiral smectic) phase occurs. This phase, the "TGB_C", is a highly dislocated version of Smectic-C. According to the deGennes analogy, this phase corresponds to Abrikosov's flux lattice when the Ginzburg parameter κ is negative. We also show that an Ising like transition between the TGB_A and TGB_C occurs and that this phase boundary, together with the Sm-A/TGB_A, Sm-C/TGB_C, and the *x-y* like Sm-A/Sm-C* phase boundaries, meet at a multicritical point.

In the last two years much progress has been made both experimentally[1–3] and theoretically[4–6] in understanding the effect of chirality on Sm-A liquid crystals. In particular the Sm-A* phase, discovered by Goodby et al. in the highly chiral nP1M7 $n = 13, 14, 15$ has[2] been identified as the twist Grain boundary phase (TGB). The TGB is a highly dislocated Sm-A phase which, according to the deGennes analogy, corresponds to the Abrikosov flux lattice in type II superconductors.

Previously,[5] we demonstrated that chirality leads to the TGB phase in the mean field Chen-Lubensky[7] phase diagram. Here we shall argue that a second TGB phase is expected on the Sm-C side of the phase diagram. This second phase consists of a twisted stack of two dimensional slabs of Sm-C separated by grain boundaries. Furthermore we show that an Ising-like phase transition between the original TGB phase, hereafter called the TGB_A, and the new TGB phase, the "TGB_C", can occur.

To understand the TGB phases, it is useful to review the deGennes analogy[8] which is based on the two observations: (1) Both the normal to superconducting transition in metals and the NA transitions are described by a complex order

parameter. In the case of the NA transition, this order parameter is defined in terms of the mass density $\rho = \rho_0 + [\bar{\psi}(\vec{r}) \exp(iq_0 z) + c.c.]$. (2) The order parameter in both systems is coupled via covariant derivatives to some vector field. The vector field in the NA transition problem is simply the director $\hat{n}$ and it corresponds to the electromagnetic vector potential in the Ginzburg-Landau theory of superconductivity. The director is covariantly coupled to ψ in order insure rotational invariance of the deGennes free energy. Based on these considerations deGennes showed that the N–A transition could be modeled with a free energy equivalent to[5]

$$F_{\text{deGennes}} = (C_{\parallel}\hat{n}_i\hat{n}_j + C_{\perp}\delta_{ij}^{T}(\hat{n}))(D_i\psi)^*(D_j\psi) + \alpha(T - T_{NA})|\psi|^2 + \frac{g}{2}|\psi|^4 \quad (1)$$

where $\psi = \tilde{\psi} \exp(iq_0 z)$, unlike $\tilde{\psi}$, exhibits rapid spatial oscillations corresponding to the smectic layering. We have also defined $\delta_{ij}^{T}(\hat{n}) = \delta_{ij} - \hat{n}_i\hat{n}_j$ and $\tilde{D} \equiv \nabla - iq_0\hat{n}$.

The theory defined by $F_{N^*A} = F_{\text{deGennes}} + F_{\text{Frank}} + \int d^3\vec{r}\,(h\hat{n} \cdot \nabla \times \hat{n})$, where

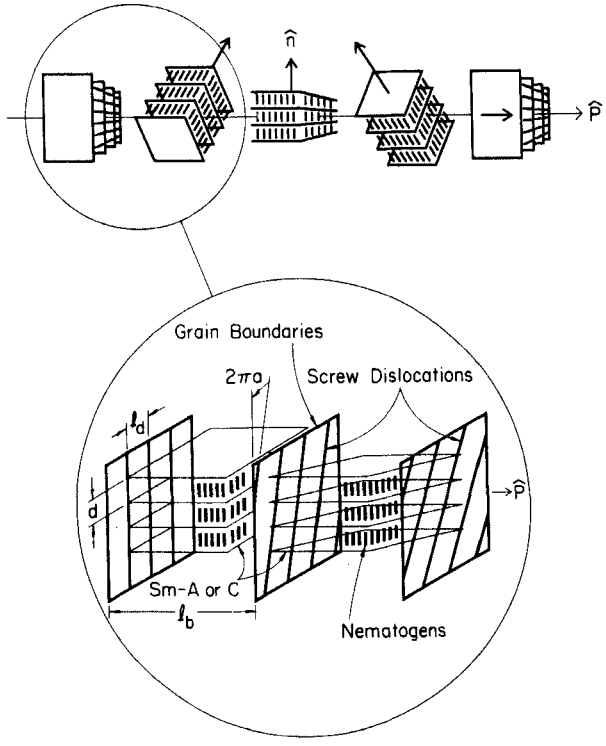

FIGURE 1 The TGB phase is a twisted array of two-dimensional smectic (Sm-A for TGB_A or Sm-C for TGB_C) slabs stacked along the pitch axis. The detailed area below shows two such slabs. The slabs are segmented by twist grain boundaries which consist of parallel dislocation lines with spacing l_d. This implies that smectic layer normals of adjacent slabs differ by an angle $2\pi\alpha \equiv d/l_d$, which also happens to be the angle between the axis of dislocations in adjacent grain boundaries. Since the director in the TGB twists in a manner essentially identical to that in the cholesteric phase, it follows that $2\pi\alpha = k_0 l_b$ where l_b is the spacing between grain boundaries and $2\pi/k_0$ is the pitch length.

h is the chirality, provides the basis for theoretical discussions of the cholesteric to Sm-A transition. In particular, one may use it to show that the cholesteric twist is partially or entirely expelled upon the development of smectic order.[4] Furthermore, at an interface between a cholesteric and smectic region of a sample, one expects the twist to penetrate only a distance $\lambda_2 = \sqrt{K_{2g}/(2C_\perp q_0^2|r|)}$, where $r \equiv \alpha(T - T_{NA})$, and K_2 is the twist elastic constant.

Since the analogue of the flux tube in smectic liquid crystals is the screw dislocation, one expects that there might be a highly dislocated smectic A phase. However a detailed analysis of the development of smectic layers[4] in a cholesteric reveals that the dislocations do not form a triangular lattice like the flux lattice in superconductors. Instead the dislocations line up into rows called grain boundaries (GB). The latter then stack up along the pitch xis of the cholesteric with separation $l_b \approx \sqrt{dP}$ where d is the smectic layer spacing and $P = 2\pi K_2/h$ is the cholesteric pitch length. Although the dislocation lines within a GB are parallel, dislocation lines in adjacent GB's are rotated by an angle $k_0 l_b$ about the pitch axis (see Figure 1).

Before proceeding further it will be useful to briefly consider the structure of dislocations[9] in Sm-C. Let $\vec{c} = c\,(\cos(\phi), \sin(\phi), 0)$ be the Sm-C director and let u be the layer displacement along the z axis, then using the standard Grinstein-Pelcovitz[10] free energy one may verify that at least four axially symmetric screw dislocations exist viz. $u(\vec{r}) = d/2\pi \tan^{-1}(y/x) = d\theta/(2\pi)$ and $\phi(\vec{r}) = \phi_0 + \theta$ where $\phi_0 = 0, \pm\pi/2$, or π. Because these dislocations are also disclinations they have logarithmically divergent self energies. Consequently, one expects that the dislocations will bind with antidisclinations resulting in a dipolar form for ϕ.

In a study of these dipolar dislocations, Kléman and Lejček[9] found (in a particularly tractable limit) that $\phi = 1/2\,(\phi^+ + \phi^-)$ where $\phi^\pm \propto \bar{x}\{\bar{x}^2 + \bar{y}^2 \pm 2\beta\bar{x}\bar{y}\}^{-1}$ and where β is a constant defined in terms of model parameters. The dipolar nature of the solution is particularly manifest in the $\beta \to 0$ limit which applies as one approaches the AC boundary. They have also shown that the interaction energy of a pair of dislocations is $\sim 1/r^2$ which gives a finite GB energy $\sim 1/l_d^2$.

We now turn to the analysis of the $N^* \to TGB_C$ transition within the chiral Chen-Lubensky model. This model, introduced in Reference 5, is defined by

$$F_{CL} = F_{N^*A} + \int d^3\vec{r}\{D_\parallel|(\hat{n}\cdot\nabla - iq_0)^2\psi|^2 + D_\perp\delta_{ij}^T\delta_{kl}^T(D_iD_j\psi)(D_kD_l\psi)^*\}. \quad (2)$$

Consider the instability of the cholesteric phase with respect to the development of Smectic-C layering. An analysis closely paralleling the Sm-A layering instability theory of sec. V, Reference 4 has been performed with F_{CL} assuming $C_\perp < 0$. The results are as follows: Smectic-C layering occurs when r drops below $r_{c2} = \alpha(T_{c2}(h) - T_{NA})$ given by

$$r_{c2} = \frac{C_\perp^2}{4D_\perp} - (4D_\perp q_0^4)\left(\frac{h}{q_0K_2}\right)^{4/3} R\left(\frac{C_\perp}{4D_\perp q_0^2}, \frac{C_\parallel}{4D_\perp q_0^2}\right), \qquad -C_\perp > D_\perp q_0 k_0$$

$$= \text{const.}D_\perp q_0 k_0\left(1 + \frac{C_\parallel}{4D_\perp q_0^2}\right)^{1/2}, \qquad 0 < -C_\perp < D_\perp q_0 k_0 \quad (3)$$

where $R(x_\perp, x_\parallel) = \kappa_0[(1 + x_\parallel)x_\parallel x_\perp^2]^{1/3}$ and κ_0 is a numerical constant of order unity. This form for r_{c2} is consistent with a smooth matching of the N*/TGB$_A$ and N*/TGB$_C$ phase boundaries i.e., $\lim_{C_\perp \downarrow 0} r_{c2}(C_\perp) = \lim_{C_\perp \uparrow 0} r_{c2}(C_\perp)$. This continuity is a rigorous consequence of the continuity of the eigenvalues of the linearized Chen-Lubensky (CL) equations as $C_\perp$ changes sign.

In spite of the layering, the induced director distortion, $\delta\hat{n}$, is negligible near T_{c2} since $\delta\hat{n} = O(\psi^* \vec{D}\psi)$. Therefore near T_{c2},$\hat{n} \approx (0, \cos(k_0' x), \sin(k_0' x))$ where $2\pi/k_0' \approx 2\pi/k_0 = P$. At the instability, smectic will appear in the form of two dimensional slabs characterised by $\psi^{\pm}_{slab}(\vec{r}; \bar{x}) = \phi(x - \bar{x}) \exp(i\vec{q}_\perp^{\pm} \cdot \vec{r})$ where the smectic layering vector $\vec{q}_\perp^{\pm} = q_0(1 + O(k_0/q_0))(0, \cos(k_0\bar{x} \pm \theta), \sin(k_0\bar{x} \pm \theta))$. (See Figure 2). Here $\tan^2\theta = -C_\perp/2D_\perp q_0^2$ gives the angle θ between $\hat{n}$ and the layer normals in the bulk Sm-C. This form for ψ_{slab} means that a Sm-C slab parallel to the yz plane can appear anywhere along the pitch axis since $\bar{x}$ is arbitrary.

The layering amplitude $\phi(x - \bar{x})$ has finite width, since if $x - \bar{x}$ is large $< (\hat{q}_\perp, \hat{n}(x)) \neq \theta$. In the TGB$_A$ phase $\phi(x - \bar{x})$ was a gaussian of width $\xi_* = 1/\sqrt{q_0 k_0}$. However in the TGB$_C$ phase this function is non-gaussian. Its width

$$\xi_* = \frac{d}{2\pi}\left(\frac{q_0}{k_0}\right)^{1/3}\left(\frac{D_\perp q_0^2}{|C_\perp|}\right)^{1/6} \quad \text{if} \quad |C_\perp| >> D_\perp q_0 k_0 \tag{4}$$

decreases as $-C_\perp \downarrow 0$, until $C_\perp \approx D_\perp q_0 k_0$ where it saturates at $1/\sqrt{q_0 k_0}$, the TGB$_A$ slab width. This result, like the continuity of r_{c2}, is a rigorous consequence of the continuity of eigenfunctions of the linearized CL equations.

At the layering instability, the smectic-C slabs nucleate throughout the cholesteric until a 1-dimensional lattice of slabs forms. This is the TGB$_C$ phase. The smectic order parameter for the TGB$_C$ is $\psi(\vec{r}) = \Sigma_s \psi^{\pm}(\vec{r}; x_s) \exp i\phi_s$, where ϕ_s is the phason angle of slab s, $x_s = sl_b$, and where $l_b \sim \xi_*$. As with the TGB$_A$ the destructive

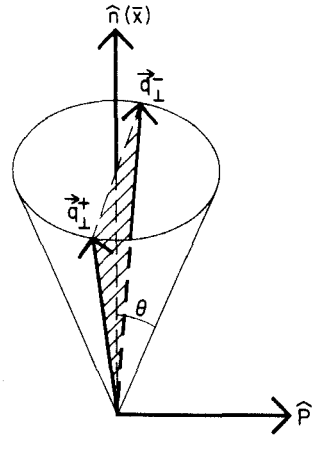

FIGURE 2 The smectic layering wavevector $\vec{q} = \vec{q}^{+}$ or $\vec{q}^{-}$. These directions were determined by (1) $< (\vec{q}, \hat{n}(\bar{x}))$ equals θ, the angle between the layer normals and $\hat{n}$ in bulk samples of smectic C, and (2) that $\vec{q}$ lies perpendicular to the pitch axis $\hat{P}$. The latter condition is required by the translation invariance of the linearized CL equations in the plane perpendicular to $\hat{P}$.

interference of the smectic order in adjacent slabs gives rise to a row of screw dislocation lines with spacing $l_d \simeq d/(k_0 l_b)$.

To prove (within mean field theory) that the TGB_C will always occur, one must demonstrate that the N*/TGB_C transition is not preempted by the direct N*/Sm-C* transition. The latter occurs at $r_{N^*C^*}$ given by[5]

$$r_{N^*C^*} = -\left(\frac{g}{K_2}\right)^{1/2} h + \frac{1}{4D_\perp q_0^4}\left[-C_\perp q_0^2 + \frac{1}{2}\left[\frac{K_2 g}{K_3^2}\right]^{1/2} h\right]^2 \tag{5}$$

where K_3 is the bend elastic constant. Using Equations (8) and (9) we find that for small h, $r_{N^*C^*} < r_{c2}$ provided

$$-C_\perp \leq (4D_\perp q_0^2)\frac{K_3}{K_2} \tag{6}$$

This is the $C_\perp < 0$ analogue of the Ginzburg criterion that the flux lattice can occur in a superconductor only when $\kappa > 1/\sqrt{2}$. The T_{c2}, T_c and (see discussion below) T_{c1} lines will meet when $C_\perp$ satisfies the equality in Equation 6.

One interesting difference between the linear T_{c2} analysis for the TGB_A and TGB_C is that the slab orientation is uniquely determined for the TGB_A. This is not the case for the TGB_C. In the TGB_C the orientation of slab s is either $\vec{q}_s^{\,+}$ or $\vec{q}_s^{\,-}$ which leaves the sign of $\vec{c}$ undetermined. (See Figure 2). However we expect that the non-linearities will remove all this degeneracy except for the sign of $\vec{c} \cdot (\vec{n} \times \hat{P})$ averaged over the sample.

As will be discussed below, the N*/TGB_A phase boundary connects with that of the N*/TGB_C transition. Hence for T just below T_{c2}, a TGB_A to TGB_C transition occurs at $C_\perp = 0$. Given the observations in the previous paragraph together with the observation that the lattice constants l_b and l_d are slowly varying as $C_\perp$ changes sign (see discussion around Equation 3) we conclude that this TGB_A/TGB_C transition is Ising like, for T near T_{c2} ($C_\perp = 0$).

We next consider the Sm-C*/TGB_C phase boundary which occurs at $T = T_{c1}(h)$ or $h = h_{c1}(T)$. In general $h_{c1} = \varepsilon_{\text{screw}}/\Phi$ where Φ is defined to be the change of the sample twist per unit length of added screw dislocation. (For a Sm-A screw dislocation $\Phi = d$). Formally one can show that the field configuration and, hence, $\varepsilon_{\text{screw}}$, Φ, h_{c1} are continuous as the thermodynamic[11] Sm-A/Sm-C* phase boundary is crossed. Therefore the Sm-A/TGB_A, SM-C*/TGB_C and thermodynamic Sm-A/Sm-C* boundaries intersect. According to the discussion in Reference 5 this occurs at $(r, C_\perp)_{T_1} = (-(2dgh/D_\perp^{1/2})^{2/3}, 1/2K_3 q_0^2\,(D_\perp g h^4/4d^2)^{1/3})$.

At the TGB_A edge of the TGB_A/Sm-A boundary, the separation between the dislocations is arbitrarily large and their interaction energy is arbitrarily small. Therefore, if one moves along this edge through the thermodynamic A/C* boundary, then TGB_A changes to TGB_C. Hence the TGB_A/TGB_C also intersects at T_1. Next observe that the intersection of the T_{c1} with the T_c line indicates that the Sm-C* $\rightarrow$ TGB_C becomes preempted by the direct Sm-C* $\rightarrow$ N*. This occurs when $C_\perp$ violates the inequality in Equation (6). The phase diagram based on these considerations is given in Figure 3. Although the nature of the TGB/Sm-C* tran-

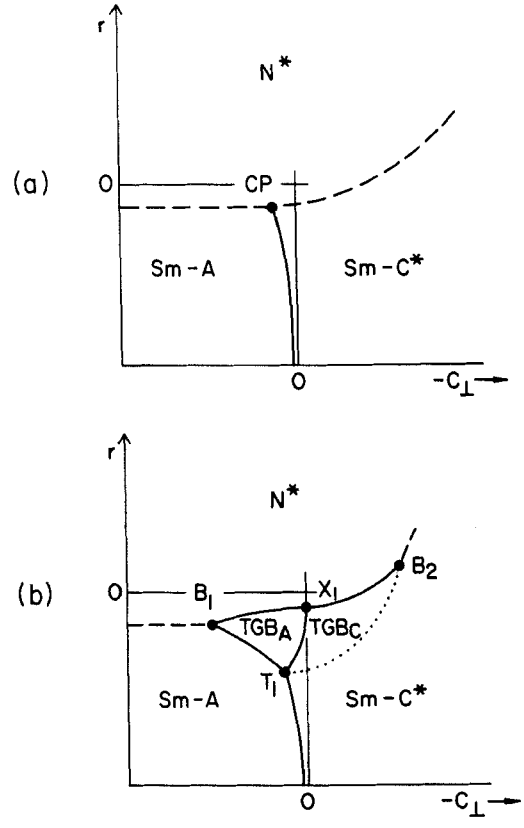

FIGURE 3 The mean field phase diagram of the chiral CL model. Two TGB phases replace the NAC point which occurs when the chirality vanishes. The TGB_A phase occurs if $k > 1/\sqrt{2}$ whereas the TGB_C phase occurs if Equation 6 is satisfied. The N*/TGB_A, TGB_A/Sm-A, Sm-A/Sm-C*, N*/TGB_C, phase boundaries are second order. The TGB_A/TGB_C transition, at least near X_1, is second order and the N*/Sm-A and the N*/Sm-C* transitions are first order. The nature of the TGB/Sm-C* transition is unknown.

sition is somewhat unclear, it is plausible that a first order TGB_C/Sm-C* or a second order TGB_{C^*}/Sm-C* transition occurs. In the latter case, a $TGB_C \rightarrow TGB_{C^*}$ transition, in which the pitch of the Sm-C* within each slab comes in from ∞, occurs at some $T < T_{c1}$. At T_{c1}, l_b and l_d would then diverge as the internal Sm-C* pitch length varies continuously.

In view of the above discussion, we hope that our experimental colleagues rise to the challenge of finding the TGB_C phase.

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11. "Thermodynamic transition" refers to the transition which would occur if the nucleation of screw dislocations were suppressed.